

## REMOVAL OF ORGANIC SULFUR FROM COAL: THE USE OF LIQUID SULFUR DIOXIDE

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### ABSTRACT

The utility of liquid  $\text{SO}_2$  for the removal of organic sulfur from several Eastern bituminous coals has been explored. Reactions were carried out in sealed fritted glass tubes at elevated temperatures; after subsequent washing, the coal was analyzed for sulfur content. Approximately 40% of the organic sulfur could be removed in these simple exploratory experiments. In addition, comminution of most of the coals occurred and a portion of the coal was extracted. The extract from selected coals was characterized by thin-layer chromatography, by nmr ( $^1\text{H}$  and  $^{13}\text{C}$ ) and infrared spectroscopy, and by field-ionization mass spectrometry. For comparison, extractions with phenol and *p*-cresol, under similar conditions, were also examined. The results of these preliminary investigations warrant further research to establish optimum conditions for the removal of sulfur compounds from coal by treatment with liquid  $\text{SO}_2$  and to facilitate removal of residual  $\text{SO}_2$  from the coal.

### INTRODUCTION

Solvent extraction has been extensively used for compositional characterization of coals.<sup>1,2</sup> Several existing coal refining processes<sup>3-5</sup> use solvent treatment, along with pressurized hydrogen to facilitate some degree of desulfurization. Treatment with liquid  $\text{SO}_2$  has been successfully used to remove organic sulfur compounds from petroleum on a commercial scale.<sup>6</sup> The ability of liquid  $\text{SO}_2$  to disintegrate various coals has been exploited to produce low-sulfur coal powders via release of pyrite.<sup>7</sup> Utilization of liquid  $\text{SO}_2$  treatment of coal for the removal of organic sulfur, however, has not been investigated. In this paper we report the results of a set of preliminary experiments in which the effectiveness of liquid  $\text{SO}_2$  for removal of organic sulfur from bituminous coals PSOC 194, 267, 270, and 319 was investigated.

### EXPERIMENTAL

Procedures for the manipulation and preparation of the sulfur dioxide (Matheson, anhydrous) have been described previously.<sup>8,9</sup> Coal samples were obtained from the Coal Research Section, Pennsylvania State University. All other materials were of commercial origin and used as received.

Reactions were carried out in borosilicate glass tubes fitted with a medium-porosity fritted glass filter to provide two chambers of ca. 20 mL capacity each. The chambers were terminated with glass tubing of different sizes: one end permitted introduction of lump (ca. 1 cm) coal and the other end facilitated easy sealing under vacuum. For reactions at elevated temperatures, these tubes were placed in a Parr model 4641 autoclave reactor.

In a typical experiment, the reaction tube was charged with a coal sample (ca. 5 g) sealed on one end, and thoroughly evacuated. After distillation of sulfur dioxide (ca. 8 mL) into the tube at  $-78^{\circ}\text{C}$ , the reaction tube was cooled to  $-196^{\circ}\text{C}$  and sealed at the other end. Upon warming to room temperature, the tube, along with others, was placed in the autoclave and the autoclave was evacuated. The autoclave was then charged with ca. 100 mL of liquid  $\text{SO}_2$  to provide backing pressure for the reaction tubes at elevated temperatures, closed, and heated at ca.  $4^{\circ}\text{C}/\text{min}$  to the reaction temperature. After maintenance of the reaction temperature for 60 min, the autoclave was cooled, depressurized, and opened. Each reaction tube was then inverted in a cold bath at  $-78^{\circ}\text{C}$  to separate the liquid  $\text{SO}_2$  from the coal by filtration via the internal frit. The red to orange colored liquid  $\text{SO}_2$  solution was frozen, the tube was opened, the coal was transferred to another container, and all volatile materials were allowed to evaporate over a two hour period. The viscous, oily extract remaining after evaporation of the liquid  $\text{SO}_2$  was retained for subsequent analysis. The treated coal was washed for analytical purposes in a Buchner funnel with sequential aliquots of distilled water, acetone, water, 3.8 M nitric acid, water, and acetone until no yellow color was observed in each wash liquid. The coal was then dried at  $110^{\circ}\text{C}$  and analyzed for sulfur. In separate washing experiments with the raw coals, no yellow color was observed in the wash liquids; subsequent sulfur analyses of the coal indicated that only inorganic sulfur was removed from the raw coal by this wash procedure.

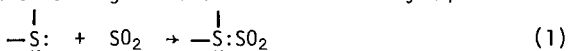
For comparison of the results of these coal/liquid  $\text{SO}_2$  experiments, two other types of experiments were also run. Authentic samples of iron pyrite were treated with liquid  $\text{SO}_2$  and liquid  $\text{SO}_2/\text{H}_2\text{O}$  mixtures at  $100^{\circ}\text{C}$  using procedures analogous to those described above; no apparent reaction occurred. Samples (ca. 4 g) of PSOC 267 were treated with 10 mL of phenol and p-cresol in sealed tubes at  $181^{\circ}$  and  $200^{\circ}\text{C}$ , respectively. The coal was subsequently washed in a Buchner funnel with distilled water and acetone, dried at  $110^{\circ}\text{C}$ , and analyzed for sulfur.

All sulfur analyses, at least in triplicate, were accomplished with a Fisher model 470 sulfur analyser. Field-ionization mass spectra were obtained on a Varian model MAT CH5 spectrometer with sample temperatures from  $120^{\circ}$ – $280^{\circ}\text{C}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were recorded on a JEOL FX90Q Fourier transform spectrometer fitted with a broadband probe and deuterium lock. Samples were in  $\text{CDCl}_3$  solution with internal TMS reference. Infrared spectra of the extract (thin film on NaCl plates) were recorded on a Perkin Elmer model 621 spectrometer. Thin-layer chromatography of the extract was carried out with the nmr sample solutions using silica gel (Si-30) plates. Elution was accomplished with 10% acetone/hexane, 30% acetone/hexane, and absolute ethanol; either  $\text{I}_2$  vapor or phosphomolybdic acid (5% w/v in ethanol) was used to develop the plates.

## RESULTS AND DISCUSSION

Precombustion desulfurization of coal has been a topic of immense interest and importance<sup>10,11</sup> since it offers an alternative to installation and operation of expensive post-combustion scrubbers for conventional combustion systems. Although a variety of processes are available for precombustion removal of inorganic sulfur compounds, practical procedures for removal of covalently bound organic sulfur are relatively uncommon. Thus, application of novel chemical approaches to the problem would appear to be appropriate. Early reports<sup>12</sup> of the ability of liquid SO<sub>2</sub> to disintegrate a variety of coals and to extract a portion of the coal along with our previous experience with this solvent suggested investigation of the utility of liquid SO<sub>2</sub> as a means of removing organic sulfur from coal. If successful, such a procedure would utilize a pollutant to remove the source of that pollutant.

Liquid sulfur dioxide is recognized as an excellent solvent for aromatic, heterocyclic, and alkyl sulfides<sup>8</sup> which can be derived from coal.<sup>1,2,13</sup> As a liquid, SO<sub>2</sub> is not easily oxidized or reduced and the adducts responsible for its solvent properties are both thermally and hydrolytically labile;<sup>8</sup> thus any contamination of the coal by residual sulfur dioxide should be readily eliminated. Although other interactions and reactions will be considered in future reports, only reactions based on the mild Lewis acid characteristics of liquid SO<sub>2</sub> are of importance here. Thus, the reaction of significance is summarized by Eq.1:



Products from this reaction are usually highly colored and highly soluble in liquid SO<sub>2</sub>.<sup>8</sup> Physical disintegration of the coal by liquid SO<sub>2</sub>, probably via similar donor-acceptor reactions with aromatic, amine, and oxygen containing functional groups, would serve to promote the reaction in Eq.1. It should be emphasized that frequently, the chemical properties of liquid SO<sub>2</sub> can be significantly altered by the presence of cosolvents;<sup>8</sup> often, undesirable side reactions occur in such mixed media.

The characteristics of the bituminous coals utilized in these preliminary investigations are given in Table I; our sulfur analyses are given in parentheses. PSOC 267 and 270 were chosen since they contain significant amounts of organic sulfur but little pyritic sulfur which might confuse interpretation of preliminary results. Our analyses of PSOC 270 reveal that, although the lumps in our sample had the composition indicated in Table I, the fines in our sample had a sulfur content of ca. 6% with the additional sulfur being pyritic. All results reported here concern the lump coal of PSOC 270. For comparison, PSOC 194 which contains both pyritic and organic sulfur and PSOC 319 which contains only pyritic sulfur were also examined. Use of the fritted glass reaction tubes facilitated observation of reactions, isolation of the extracted material, and rapid examination of several coals and reaction conditions.

The results are summarized in Table II. At room temperature, liquid SO<sub>2</sub> readily wets each of the coals and begins to develop a yellow color upon contact. The yellow color becomes more intense upon standing and changes to intense orange or red-orange after heating. The color indicates the dissolution of donor-acceptor compounds formed between the solvent and coal constituents; the increasing intensity accompanies

an increasing concentration of these adducts. Disintegration of coal lumps was observed for PSOC 267, 270, and 319; the extent of disintegration increases progressively in the order listed. Although lumps of PSOC 194 were not disintegrated, close examination revealed appreciable swelling and expansion along fissures. It should be realized that the only mechanical agitation used during these experiments was a mild shaking of the tubes to initially mix the materials. At this stage, there does not appear to be an obvious pattern which links maceral content to degree of disintegration.

Inspection of Table II reveals that significant amounts of  $\text{SO}_2$  are retained on the coal (Exp. 1). Effective removal of this residual  $\text{SO}_2$  is essential. Mild heating ( $110^\circ\text{C}$ ) and washing with water or aqueous detergent solutions were less effective than the wash solution used in Exp. 2. When used alone, organic solvents are more effective than mineral acid or base (compare Exp. 2 and 3 with Exp. 4, 5, and 6). The utility of washing with the organic liquids for removal of the yellow  $\text{SO}_2$  adducts increases in the order: hexane, benzene,  $\text{CCl}_4$ , ethanol, and acetone. A sequence of washes using acetone, water, and  $\text{HNO}_3$  (Exp. 7) effectively removes the residual  $\text{SO}_2$  in most cases. Since the wash sequence was carried out during a filtration operation contact time with the  $\text{HNO}_3$  was insufficient to appreciably modify the coal material itself; separate wash experiments using the acetone, water,  $\text{HNO}_3$  sequence with the raw coal (PSOC 267 and 270) itself indicated that no appreciable mass change occurred and that no yellow materials were obtained under these wash conditions. Where pyrite is not present, the sulfur content of the coal after this wash sequence represents the organic sulfur remaining in the coal after the liquid  $\text{SO}_2$  treatment. For PSOC 267 and 270, ca. 37% and 25%, respectively, of the organic sulfur can be removed by simple treatment of the lump coal with liquid  $\text{SO}_2$ . Grinding the lump coal PSOC 270 (-60 mesh) improves the percentage organic sulfur removal to ca. 48%. Present results with coals containing pyrite are less easily interpreted since the wash sequence probably does not completely remove the pyrite. Furthermore, in separate experiments with authentic pyrite samples, it was demonstrated that neither liquid  $\text{SO}_2$  nor liquid  $\text{SO}_2/\text{H}_2\text{O}$  mixtures react with pyrite. For PSOC 319, where virtually all the sulfur is pyritic, the measured value of 1.6% sulfur after  $\text{SO}_2$  treatment probably represents pyrite which is not removed in the wash sequence. For PSOC 194, the measured value of 2.1% sulfur after liquid  $\text{SO}_2$  treatment more than likely represents both unreacted organic and pyritic sulfur. With PSOC 194, the failure of liquid  $\text{SO}_2$  to disintegrate the coal probably limited extraction of the organic sulfur by the  $\text{SO}_2$ .

Extraction of powdered PSOC 267 with phenol and *p*-cresol resulted in 52% and 66%, respectively, removal of organic sulfur compared to 37% by liquid  $\text{SO}_2$ . The results of the extractions with phenol and *p*-cresol are similar to those reported elsewhere for other coals.

Although these results with liquid  $\text{SO}_2$  are not as impressive as those with phenol and *p*-cresol, it has been demonstrated that organic sulfur can be removed by extraction with liquid  $\text{SO}_2$ . It is also important to note that optimum conditions for liquid  $\text{SO}_2$  extraction and for residual  $\text{SO}_2$  removal have as yet to be established. Furthermore, these preliminary results when compared with other worker's results<sup>10</sup> for a variety of organic solvents, are sufficiently encouraging to indicate that treatment with liquid  $\text{SO}_2$  should be investigated further. Experiments to define conditions

more carefully and to investigate the use of appropriate reagents that will enhance the removal of sulfur compounds from coal by liquid  $\text{SO}_2$  are underway.

The material obtained by evaporation of the  $\text{SO}_2$  extraction liquid comprises 5-10% of the original coal. Most of this oily extract dissolves in chloroform, acetone, and concentrated HCl; this material is only partially soluble in benzene and is insoluble in hexane. Very finely divided particulate matter, observed to be in suspension in the chloroform and acetone solutions appears to resemble high molecular weight material obtained by Larsen and Choudhury<sup>13</sup> during their investigation of the effectiveness of coal depolymerization reactions. Although it is likely that liquid  $\text{SO}_2$  under these conditions merely extracts lower molecular weight material already in the coal, some small degree of depolymerization could also be occurring.

Thin-layer chromatography of the liquid  $\text{SO}_2$  extract from PSOC 267 was carried out using a chloroform solution for deposition and eluted with progressively more polar solvents; long-wavelength UV illumination was used to observe fluorescence in the samples. Although no distinct bands were developed upon elution, three definite fractions that differ by polarity of constituents were apparent on the plates. Several conclusions can be drawn from these TLC experiments. The complete sample contains easily oxidizable functions. All alkyl functions are attached to aromatic residues. The less conjugated (blue fluorescent) fraction is less polar than the more conjugated (orange fluorescent) fraction. A very polar fraction, not transported by any eluent used, is even more highly conjugated (red fluorescent). These observations are consistent with the types of structures<sup>14</sup> known to exist in coals as well as with the spectroscopic measurements to be described next.

The field ionization mass spectrum of the liquid  $\text{SO}_2$  extract from PSOC 267 is illustrated in Fig. 1; the corresponding spectrum of the extract from PSOC 270 is similar in several features. The molecular weight distribution in these spectra are not as broad nor is the average molecular weight as high as might have been expected.<sup>14</sup> The presence of very finely divided particulate matter, which presumably has higher molecular weight components that are not volatilized under the measurement conditions, could be responsible for such observations. The spectra contain striking patterns in which the mass difference among major components is 14 amu. These patterns suggest the presence of a variety of  $\text{CH}_2$  containing structures. It is tempting to assign another pattern near  $m/e = 184$  to dibenzothiophene since it strongly resembles that obtained with an authentic dibenzothiophene sample. The lack of high resolution mass spectral data, however, makes such an assignment pure speculation at this stage.

The infrared spectrum of the liquid  $\text{SO}_2$  extract of PSOC 267 (neat, thin film) is shown in Fig. 2. It is apparent that the extract contains O-H, N-H, aromatic and aliphatic C-H groups, a variety of substituted aromatic structures, and probably ethers. There is no evidence of either residual  $\text{SO}_2$  or of organic structures containing  $\text{SO}_2$  substitution; no procedures other than evaporation of the liquid  $\text{SO}_2$  under ambient conditions were used to process this extract.

Proton and  $^{13}\text{C}$  (proton noise decoupled) nmr spectra of the liquid  $\text{SO}_2$  extract of PSOC 267 are shown in Fig. 3. Qualitatively, the proton spectrum resembles that of  $\text{CS}_2$  extracts of other bituminous coals as reported by Retcofsky and Friedel;<sup>15</sup> our assignments follow those of these workers. The signals with  $\delta < 1.8$  are assignable to alkyl type protons, those with  $2.0 < \delta < 3.5$  are assignable to benzylic type protons and those with  $6.9 < \delta < 8.8$  are assignable to aromatic type protons; the signal at  $\delta$  ca. 4.8 is attributed to phenolic and alcoholic type protons. Integrated intensities provide the following distribution of protons: 20.9% aromatic, 1.9% -OH, 32.1% benzylic, and 45.1% other alkyl types. It would appear that the alkyl-H/aromatic-H ratio is higher for this extract than for  $\text{CS}_2$  extracts of bituminous coals with similar carbon content (84.6% C in PSOC 267).

The  $^{13}\text{C}$  nmr spectrum reveals further detail concerning the types of structures found in the liquid  $\text{SO}_2$  extract of PSOC 267 since assignments are readily made by reference to the work of Fischer *et al.*<sup>16</sup> Features in common with both SRC extracts and methylnaphthalene extracts of bituminous coal are found in the liquid  $\text{SO}_2$  extract. The sharp signal at 14.1 ppm is assigned to terminal methyl groups on aliphatic side chains, that at 19.8 ppm to unhindered aryl methyl groups, and those at 22.7 and 31.9 ppm to  $\alpha$  and  $\beta$  methylene carbons, respectively, on tetralin type structures. The sharp, dominant resonance at 29.7 ppm is readily assigned to methylene carbons in  $\text{Ar-CH}_2\text{-CH}_2\text{-Ar'}$  groups whereas the weaker signals at 32.6, 37.4, and 39.2 ppm are characteristic of single methylene carbons bridging aromatic structures. The broad, low field band with a higher field asymmetry is typical of a composite of aromatic type carbons. Individual sharp signals within this band correspond to alternate polynuclear aromatics that are partially substituted.<sup>16</sup> The apparent absence of signals at even lower fields from carbon atoms without proton substituents is attributed to lack of NOE enhancement for these nuclei.

Thus the liquid  $\text{SO}_2$  extract of PSOC 267 has been shown to contain coal constituents similar to those obtained by extraction with common organic solvents. Although an abundance of alkyl groups (methyl and especially methylene) is found in the carbon structures as illustrated by the infrared,  $^{13}\text{C}$  nmr, and mass spectra, it is not clear whether this is representative of PSOC 267 composition or is a consequence of the properties of liquid  $\text{SO}_2$ . Less is known about the composition of heteroatom compounds in the extract: OH, NH and probably ether groups are apparent but available spectral data do not reveal other groups such as might be found in organic sulfur compounds. Unfortunately, the spectra obtained are not sensitive to divalent sulfur containing organic structures and reliable elemental analyses were precluded by lack of sufficient material. Since better characterization of this extract may eventually provide clues concerning the ability of liquid  $\text{SO}_2$  to remove organic sulfur compounds, such efforts are to be made.

In summary, preliminary experiments have demonstrated that liquid  $\text{SO}_2$  can be used to remove organic type sulfur compounds from bituminous coals and that the liquid  $\text{SO}_2$  extract contains coal components similar to those found by extraction with organic solvents. The ability of liquid  $\text{SO}_2$  to disintegrate some coals and to fracture others has been confirmed. Conditions to optimize the removal of sulfur compounds from coal and to facilitate removal of residual  $\text{SO}_2$  from the coal are under investigation.

#### ACKNOWLEDGEMENTS

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TABLE 1. Characteristics of Bituminous Coals Treated with Liquid SO<sub>2</sub>

	COAL (PSOC NO.)			
	194	267	270	319
Type	HVB	HVA	HVA	LV
Origin	OH	VA	AL	PA
Macerals (%/v)				
Vitrinite	73.3	60.9	68.1	85.5
P. Vitrinite	12.6	5.3	3.2	4.2
Micrinite	3.3	15.6	9.1	1.0
Fusinite	2.2	8.7	8.6	4.3
S. Fusinite	2.3	3.4	4.6	4.0
Resinite	3.6	1.5	0.8	0.0
Sporinite	1.8	3.2	5.0	0.5
Elemental Analysis (DAF)				
%C	78.23	84.63	83.34	86.49
%H	5.56	5.58	5.55	4.57
%N	1.72	2.53	1.74	1.61
%O(diff)	10.97	5.18	6.59	0.16
%S(total)	3.51	2.08 (1.967) <sup>a</sup>	2.77 (2.682) <sup>a</sup>	7.17
organic	1.26	2.01	2.70	0.10
pyritic	2.19	0.02	0.02	7.00
sulfatic	0.07	0.05	0.05	0.07

<sup>a</sup>Analyses done in this work.

TABLE 2. Experimental Results

Sample (PSOC No.)	Exp. No.	Solvent <sup>a</sup>	Reaction Temp. (°C)	Wash	%S	Organic Sulfur Removed
270						
lump	1	SO <sub>2</sub>	150	-	5.756	
lump	2	SO <sub>2</sub>	150	1.5M NaOH, H <sub>2</sub> O	3.802	
lump	3	SO <sub>2</sub>	150	3M HCl, H <sub>2</sub> O	3.522	
lump	4	SO <sub>2</sub>	150	H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub>	2.682	
lump	5	SO <sub>2</sub>	100	CCl <sub>4</sub>	2.602	
lump	6	SO <sub>2</sub>	100	acetone	2.316	
lump	7	SO <sub>2</sub>	150	multiple <sup>b</sup>	2.005	25%
lump	8	SO <sub>2</sub> /C <sub>6</sub> H <sub>6</sub> <sup>c</sup>	100	-	3.089	
lump	9	SO <sub>2</sub> /C <sub>6</sub> H <sub>6</sub> <sup>c</sup>	100	multiple <sup>b</sup>	1.992	25%
powder <sup>d</sup>	10	SO <sub>2</sub>	75	multiple <sup>b</sup>	1.397	48%
267						
lump	11	SO <sub>2</sub>	75	multiple <sup>b</sup>	1.241	37%
powder <sup>d</sup>	12	phenol	180	H <sub>2</sub> O, acetone	0.9394	52%
powder <sup>d</sup>	13	p-cresol	200	H <sub>2</sub> O, acetone	0.6580	66%
194						
lump	14	SO <sub>2</sub>	100	multiple <sup>b</sup>	2.134	
314						
lump	15	SO <sub>2</sub>	100	multiple <sup>b</sup>	1.584	

a. For liquid SO<sub>2</sub> reactions, 60 min reaction time was used and for organic solvent reactions, 5 hr was used.

b. The multiple wash consisted of the use of sequential aliquots of acetone, H<sub>2</sub>O, 3.8 M HNO<sub>3</sub>, H<sub>2</sub>O, acetone (see text).

c. The SO<sub>2</sub>/benzene solution was ca. 1:1 (vol).

d. Lump coal was crushed and ground to -60 mesh.

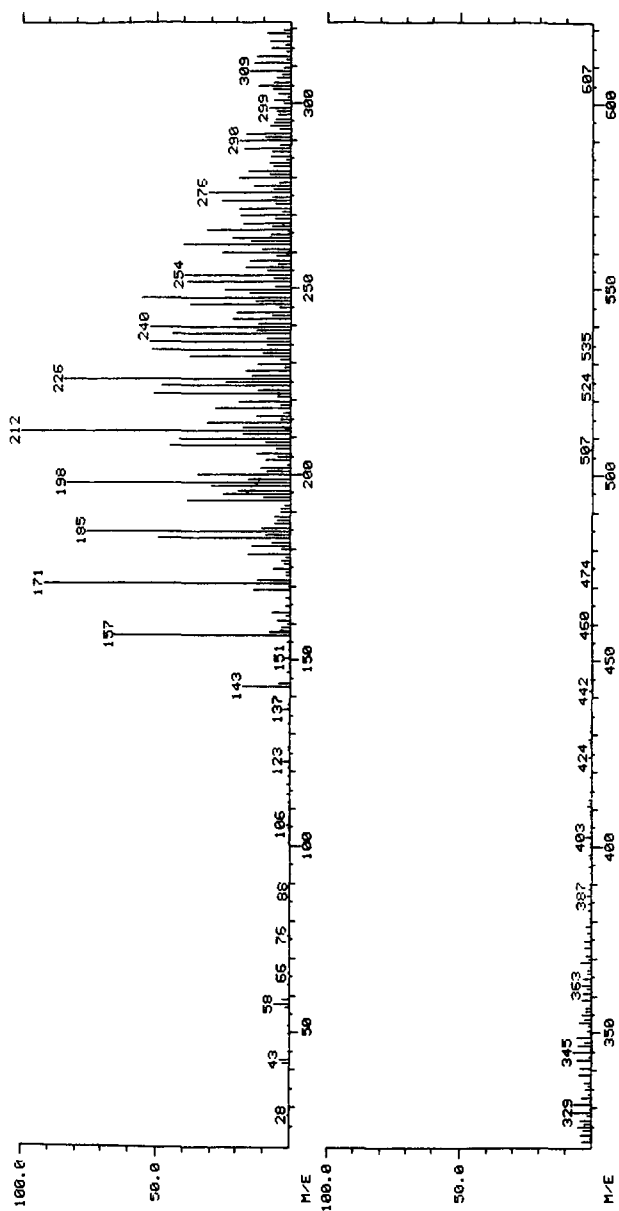


FIGURE 1. Field ionization mass spectrum of the liquid SO<sub>2</sub> extract of coal PSOC 267.

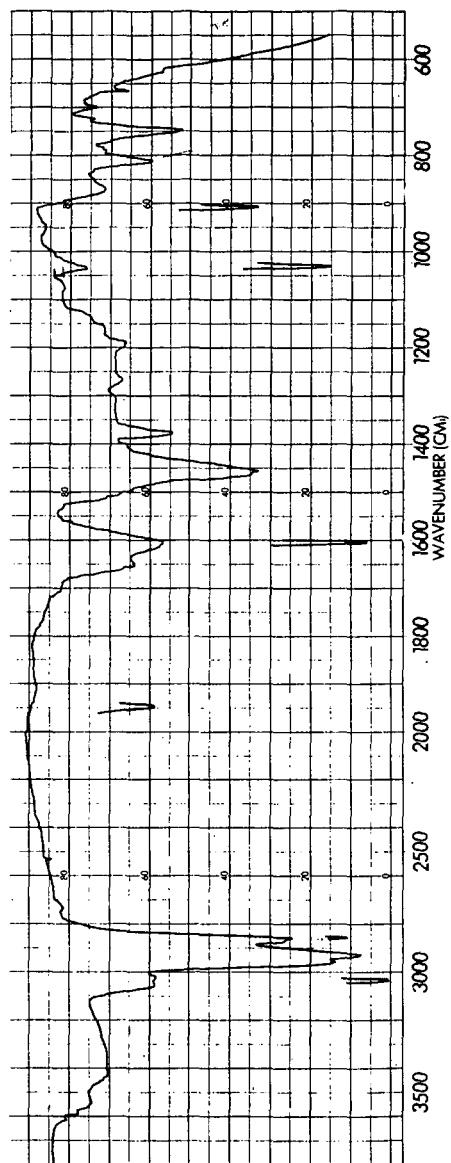


FIGURE 2. Infrared spectrum of the liquid SO<sub>2</sub> extract of coal PSOC 267.

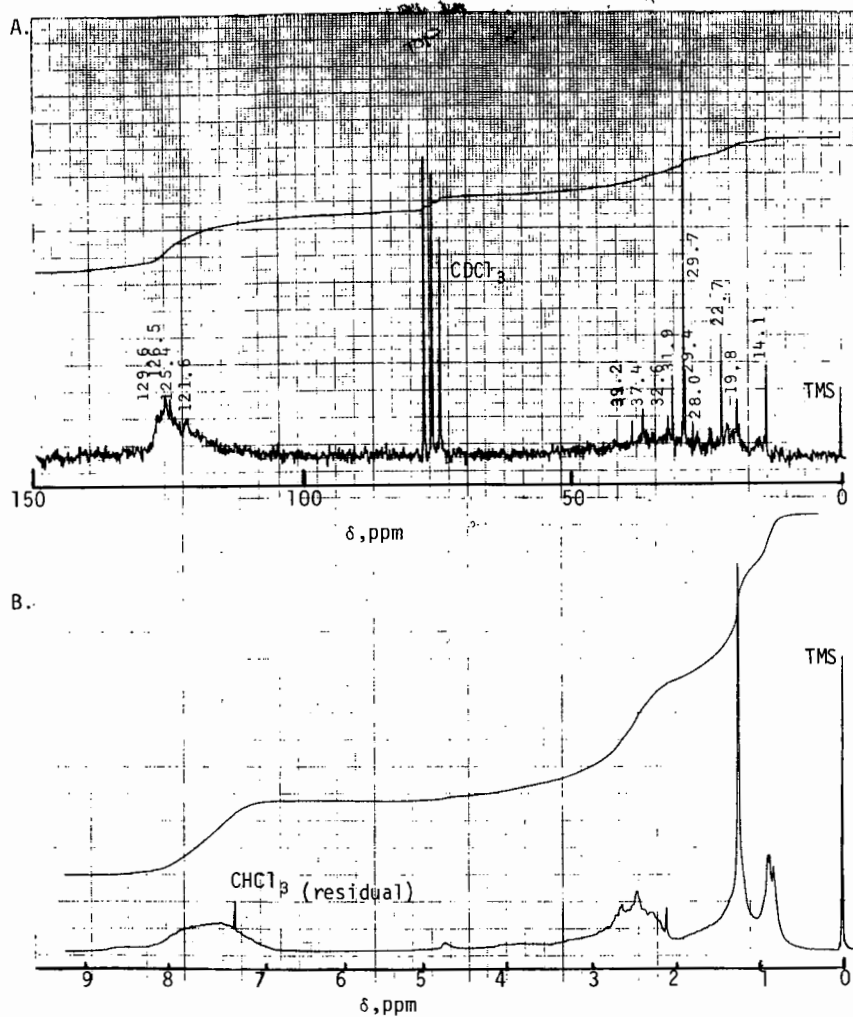


FIGURE 3. Nuclear magnetic resonance spectra of the liquid  $\text{SO}_2$  extract of coal PSOC 267 ( $\text{CDCl}_3$  solution, 5 mm tube). A.  $^{13}\text{C}$  nmr spectrum, proton noise decoupled, 2000 pulses B.  $^1\text{H}$  nmr spectrum, 10 pulses.